EPA
United States
Environmental Protection
Agency

Federal Reference Methods for NO_y, p-SO_4 and SO_2 for a Combined NO_x and SO_x Secondary NAAQS

Russell W. Long and Fred Dimmick

Office of Research and Development
National Exposure Research Laboratory, Human Exposure and Atmospheric Sciences Division

February 16, 2011

Outline

- Introduction
- Charge Questions
- Background
  - CASTNET Filter Pack (FP) Method
  - CASTNET DQI
- SO_2 FRM
  - CASTNET FP Method
  - UVF Method (SO_2 primary FRM)
- p-SO_4 FRM
  - CASTNET FP Method
- NO_y FRM
  - MOLYCON/Chemiluminescence Method

Introduction

- **Problem**
  - Establish FRMs for NO_x/SO_x NAAQS with limited resources
- **Approach**
  - Describe capabilities of readily available methods
  - Develop methods only where needed
- **Results**
  - Existing SO_2 FRM (primary NAAQS)
  - CASTNET filter pack method for SO_x
  - Study/document NO_y continuous methods
- **Impact/Status**
  - Looking for CASAC thoughts: approach and specifics
  - FRMs to be provided by final rule making, some work to be performed between initial and final rulemaking

Charge Questions

- What are the Panel's views on using the CASTNET FP to measure SO_2 for the purpose of providing annual average values as an indicator for the NO_x/SO_x standard?
- What are the Panel's views on using the current primary FRM (high time resolution UVF) to measure sulfur dioxide gas for the purpose of providing annual average values as an indicator for the NO_x/SO_x standard?

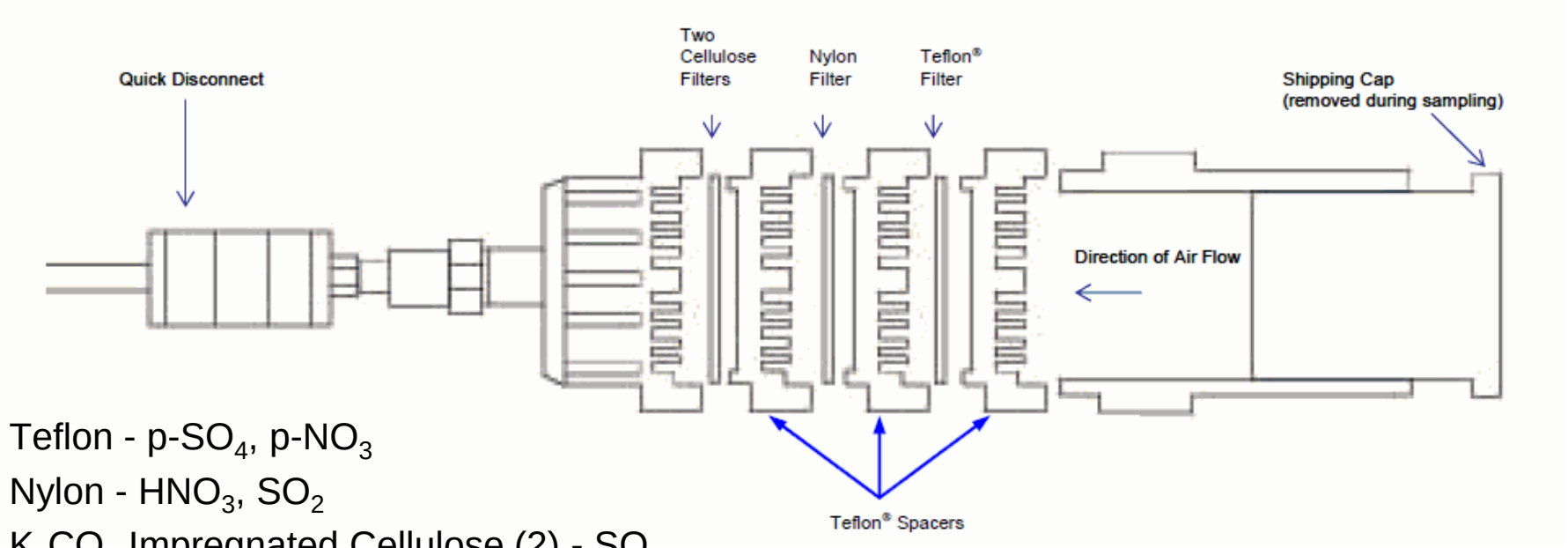
- What are the Panel's views on using the CASTNET FP to measure p-SO_4 for the purpose of providing annual average values as an indicator for the NO_x/SO_x standard?

- What are the panel's views on using CASTNET to measure t-NO_3 (p-NO_3+HNO_3) as the measurement approach for the purpose of providing annual average values to support the NO_x/SO_x standard in diagnosing NO_y instrument behavior and assist in delineating the relative fractions of contributing oxidized nitrogen species to total ambient oxidized nitrogen.

- What are the panel's views on using existing NO_y methods that are deployed, for example, in NCore as the measurement approach for NO_y for the purpose of providing annual average values as an indicator for the NO_x/SO_x standard?

CASTNET Filter Pack Method

- In use for 20+ years
- Provides weekly average concentration data
- Sample drawn at a controlled flow rate through an open-face 3-stage filter pack mounted at 10m to collect gas and particle air pollutants
- Filter extracted and analyzed by Ion Chromatography (IC)
- http://epa.gov/castnet/javaweb/docs/qapp_v6.pdf



- Teflon - p-SO_4, p-NO_3
- Nylon - HNO_3, SO_2
- K_2CO_3 Impregnated Cellulose (2) - SO_2
  - SO_2 detected as SO_4^{2-} during IC analysis

CASTNET Filter Pack Method

Table 5-1 Data Quality Indicator Criteria for CASTNET Laboratory Measurements

Analyte	Method	Precision[1] (MARPD)	Accuracy[2] (%)	Nominal Reporting Limits
Ammonium (NH_4^+)	Automated colorimetry	10	90 - 110	0.020 mg-N/L
Chloride (Cl^-)	Ion chromatography	5	95 - 105	0.020 mg/L
Nitrate (NO_3^-)	Ion chromatography	5	95 - 105	0.008 mg-N/L
Sulfate (SO_4^{2-})	Ion chromatography	5	95 - 105	0.040 mg/L

Clean Air Status and Trends Network 2008 Annual Report, U.S. Environmental Protection Agency, Office of Air and Radiation, Clean Air Markets Division, February 2010.

Table 5-3 Data Quality Indicator Criteria for CASTNET Field Measurements

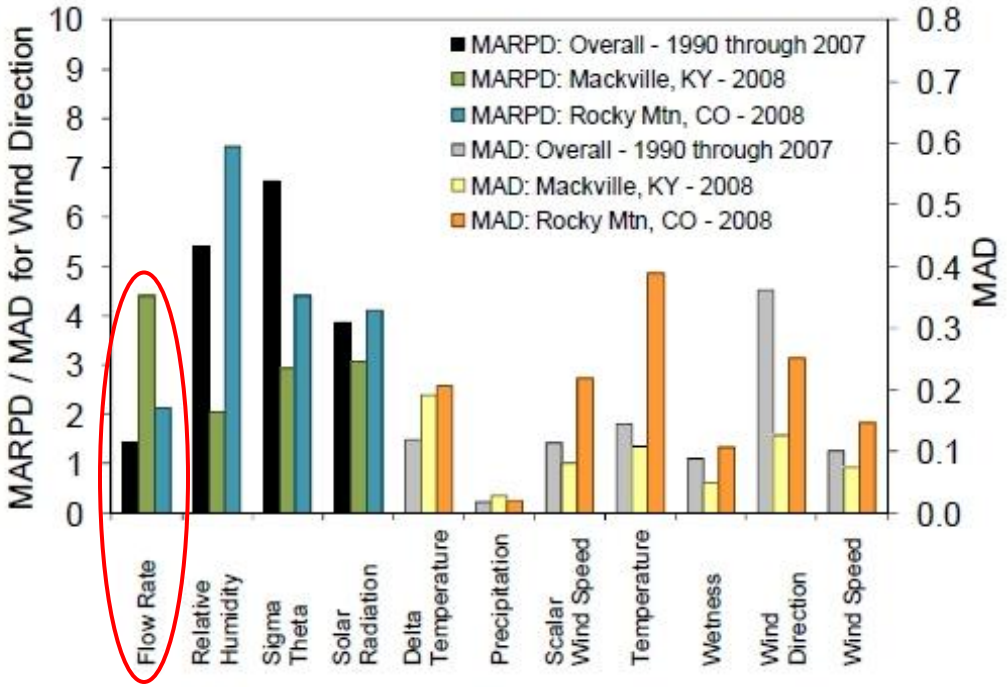
Measurement		Criteria*	
Parameter	Method	Precision	Accuracy
Wind Speed	Anemometer	± 0.5 m/s	The greater of ± 0.5 m/s for winds < 5 m/s or ± 5% for winds ≥ 5 m/s
Delta Temperature	Platinum RTD	± 0.5°C	± 0.5°C
Surface Wetness	Conductivity Bridge	Undefined	Undefined
Ozone	UV Absorbance	± 10% (of reading)	± 10%
Filter Pack Flow	Mass Flow Controller	± 10%	± 5%

Clean Air Status and Trends Network 2008 Annual Report, U.S. Environmental Protection Agency, Office of Air and Radiation, Clean Air Markets Division, February 2010.

CASTNET Filter Pack Method

United States Environmental Protection Agency

Figure 5-5 Historical and 2008 Precision Data for Continuous Measurements



Clean Air Status and Trends Network 2008 Annual Report, U.S. Environmental Protection Agency, Office of Air and Radiation, Clean Air Markets Division, February 2010.

- Precision was calculated in terms of the MARPD or mean absolute difference (MAD) of hourly measurements collected at all collocated pairs sites operated over the history of the network.
- The historical MARPD for FP flow rate met the criterion for the CASTNET filter pack measurements.

- Field accuracy results are based on instrument challenges performed using independent reference standards during site calibration visits. CASTNET sites are calibrated every six months with NIST-traceable standards. For FP flow rate, the DQI criterion were met with close to 100% frequency.

SO_2 and p-SO_4 FRM

Approach (FP)

- ORD would use the readily available and documented data, procedures and information available for the CASTNET SO_2 and p-SO_4 FP method.
- ORD will provide a technical summary of the data and supporting information and develop the basis/rationale for adopting it as an FRM.
- ORD will prepare docket materials, proposal preambles, response to comments, and the FRM in regulatory text format.

Approach (UVF)

- FRM analyzers using this UVF technique can provide the needed detection limits, precision, and accuracy and thus fulfill all purposes of an FRM. As a result, no work will be done on the current SO_2 FRM and it will be adopted as the FRM for the SO_2 indicator of the proposed secondary standard.

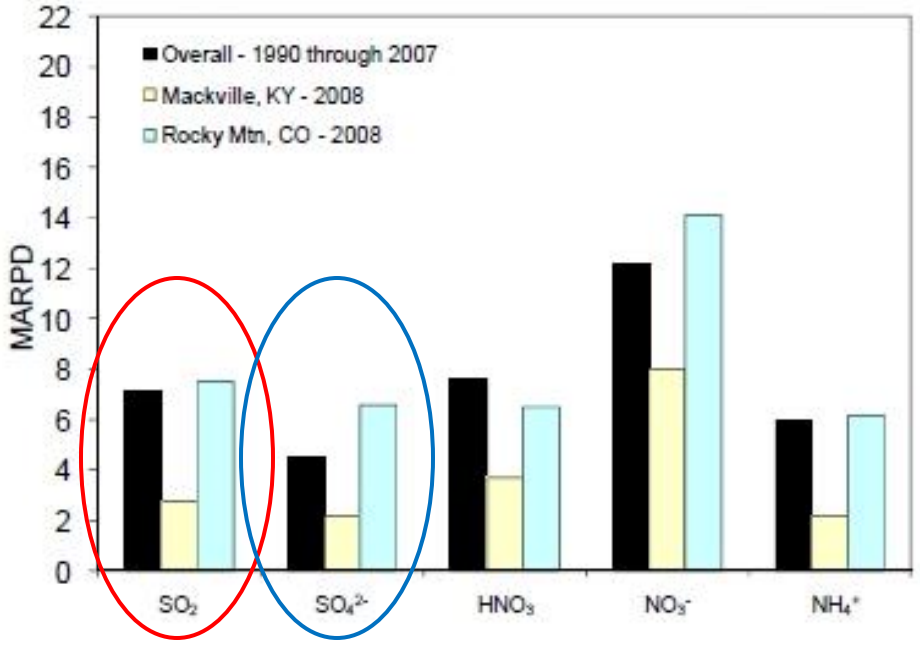
Approach (t-NO_3)

- ORD may use the substantive, readily available data and information for the FP t-NO_3 method and provide a technical summary of the data to document precision and bias of FP t-NO_3 measurements for the purpose of evaluating NO_y instrument behavior and model applications.

- What are the Panel's views of these approaches for setting the FRM?

SO_2 and p-SO_4 FRM

Figure 5-1 Historical and 2008 Precision Data for Atmospheric Concentrations



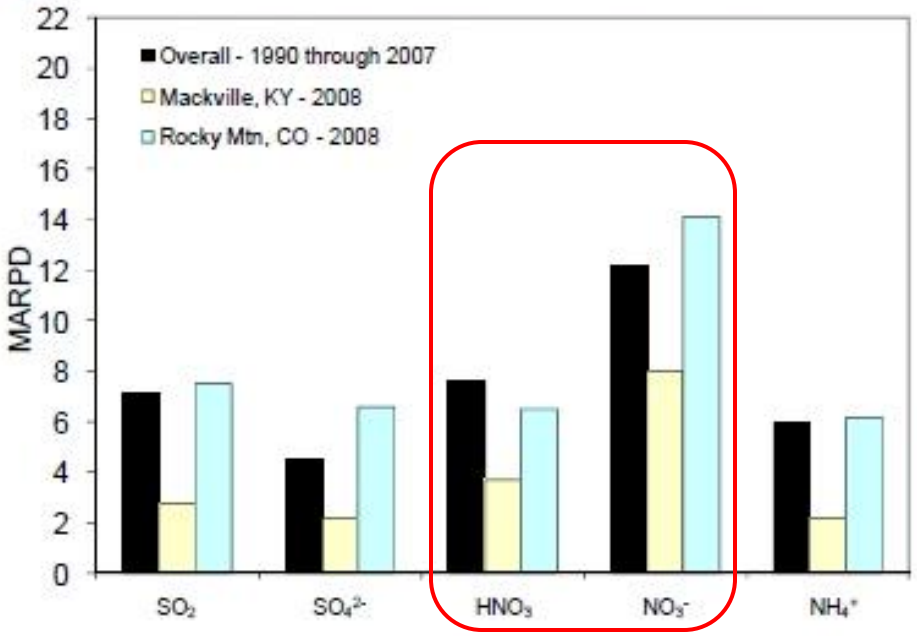
Clean Air Status and Trends Network 2008 Annual Report, U.S. Environmental Protection Agency, Office of Air and Radiation, Clean Air Markets Division, February 2010.

- The historical MARPD results for exposed filter SO_2 were above the 5 percent criterion but are considered reasonable.
- The historical MARPD for exposed filter p-SO_4 met the criterion for the CASTNET filter pack measurements.

- Laboratory precision results based upon replicate sample analysis (5%, randomly selected) meet the DQI (5% for sulfate).
- Accuracy assessed through analysis of reference and continuing calibration verification samples. Accuracy results meet the DQI (95-105% for sulfate) for both SO_2 and p-SO_4 filter media.

t-NO_3 Method

Figure 5-1 Historical and 2008 Precision Data for Atmospheric Concentrations



Clean Air Status and Trends Network 2008 Annual Report, U.S. Environmental Protection Agency, Office of Air and Radiation, Clean Air Markets Division, February 2010.

- The historical results for HNO_3 were above the 5 percent criterion but are considered reasonable.
- The results for p-NO_3 were significantly above the 5 percent goal possibly due to p-NO_3 concentrations being the lowest of all pollutants and potential sampling artifacts associated with nitrate species.
- MARPD values for t-NO_3 nitrate averaged around 6.0 over the 5 year period 2004-2008.

- Laboratory precision results based upon replicate sample analysis (5%, randomly selected) meet the DQI (5% for nitrate)
- Accuracy assessed through analysis of reference and continuing calibration verification samples. Accuracy results meet the DQI (95-105% for nitrate) for the NO_3^- filter media.

SO_2 and p-SO_4 FRMs

Schedule

- This effort began in July 2010.
- ORD is currently collecting available data and information for the SO_2, p-SO_4 methods.
- ORD will provide a technical summary of the methods data and develop the basis/rationale for making them FRMs by April 2011.
- ORD will prepare docket materials, proposal preambles and provide the FRMs in regulatory text format by the initial rulemaking date of July 2011.
- ORD will provide response to comments and the final FRMs for SO_2 and p-SO_4 in regulatory text format by the March 2012 final rule making date.

Total Reactive Nitrogen (NO_y) FRM

EPA United States Environmental Protection Agency

- What are the panel's views on using existing NO_y methods that are deployed, for example, in NCore as the measurement approach for NO_y for the purpose of providing annual average values as an indicator for the NO_x/SO_x standard?

Approach

- Upon completion of the evaluation and compilation of the generated data and information on the NO_y measurement method, ORD will be able to describe the accuracy, precision, and reliability of the NO_y instruments and their applicability as FRM.
- ORD will provide a technical summary of the data and supporting information and develop the basis/rationale for adopting it as an FRM.
- ORD will prepare docket materials, proposal preambles, response to comments, and the FRM in regulatory text format.

- What are the panel's views on ORD's assessment that additional study is needed before establishing an FRM based on the existing NO_y methods?
- What are the panel's views on the research plan for establishing existing NO_y methods as an FRM?

Total Reactive Nitrogen (NO_y) FRM

United States Environmental Protection Agency

NO_y Method Operation Principle

- Near real time, optical, direct measurement method
- Similar in principle to the Primary NO_2 FRM
- Externally located catalytic converter (Molybdenum) to convert all NO_y species to NO
  - External location of converter reduces transfer line losses of key NO_y species (i.e., HNO_3 and p-NO_3)
  - Short inlet probe to reduce loss of HNO_3, p-NO_3
- O_3-chemiluminescence detection
- 3 commercially available NO_y instruments for evaluation
  - Teledyne API Model T200U/200EU NO_y analyzer
  - Thermo Scientific Model 42i-Y NO_y Analyzer
  - American Ecotech Model EC9843 Total Reactive Nitrogen Oxides Analyzer

Total Reactive Nitrogen (NO_y) FRM

United States Environmental Protection Agency

Key Unresolved Science Questions

- **Data Quality Objectives** - Is the NO_y method capable of meeting the DQOs developed by EPA and documented in 40 CFR Part 58, Appendix A?
- **Total NO_y capture** - Is method capable of capturing all components of NO_y (HNO_3, p-NO_3)?
- **Converter efficiency**
  - MOLYCON efficiency is well established for NO_2.
  - What is the MOLYCON efficiency for other components of NO_y?
  - What is the effect of time, differing NO_y compositions and atmospheric conditions on the MOLYCON efficiency?
- **Inlet placement** - At what height should inlet be placed to eliminate vertical concentration gradient associated biases?
- **Interferences** - What species and to extent interfere with the NO_y determination?
- **Calibration/challenge procedures** – What calibration and performance challenge criteria will best represent the mixture of NO_y species that are expected to be present in the various air sheds across the U.S.?

Total Reactive Nitrogen (NO_y) FRM

Technical Approach

- **Quantify overall uncertainties associated with the NO_y method**
  - Collocated pair sampling to determine precision, bias and comparability between identical instruments under laboratory and ambient conditions.
  - The laboratory based studies will allow these figures of merit to be determined for individual NO_y species and various NO_y mixes under controlled laboratory conditions using simulated NO_y species.
  - The ambient studies will result in an assessment of precision, bias, and comparability under conditions that the FRMs would experience upon routine deployment.
  - All ambient air studies will be conducted at the AIRS sampling site on EPAs RTP, NC campus as it is anticipated that this site is representative of the proposed sites in the NO_x and SO_x combined secondary standard network.

Total Reactive Nitrogen (NO_y) FRM

Technical Approach

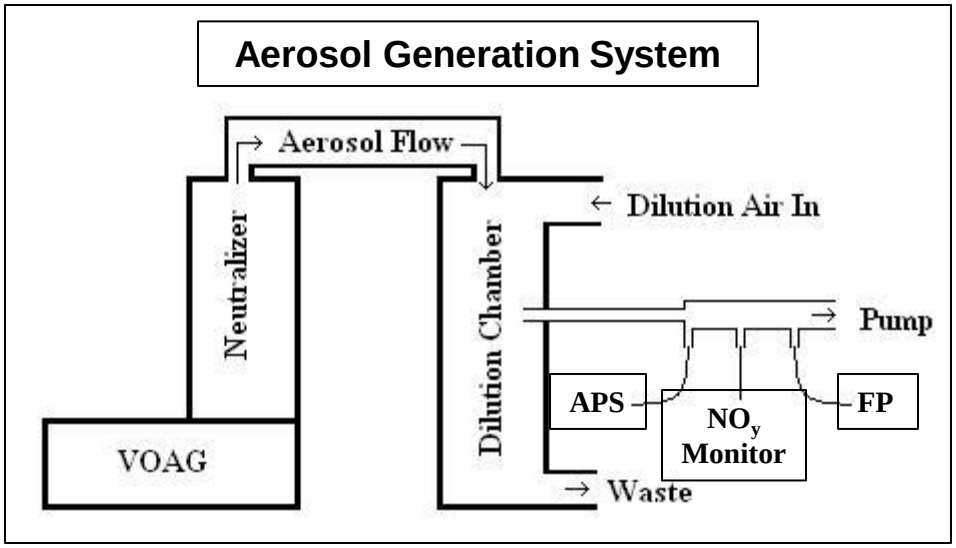
Identify and quantify NOy method interferences and measurement challenges

- Potential measurement challenges and interferences will be identified, quantified and documented through rigorous laboratory based and ambient method evaluations.
- Laboratory based studies
  - Performed under controlled conditions with simulated pollutants
  - NO_y capture (inlet and sampling losses)
  - MOLYCON efficiency and stability with respect to individual NO_y species and total NO_y
  - Measurement interferences of other atmospherically relevant species in the NO_y determination
- Ambient studies
  - Used to confirm laboratory findings under conditions that the potential FRMs will experience upon deployment
  - NO_y speciated into its individual components and summed for comparison with results obtained from the candidate methods allowing for the assessment of the capability of the method in determining NO_y as an FRM and identify any sampling shortcomings.

Total Reactive Nitrogen (NO_y) FRM

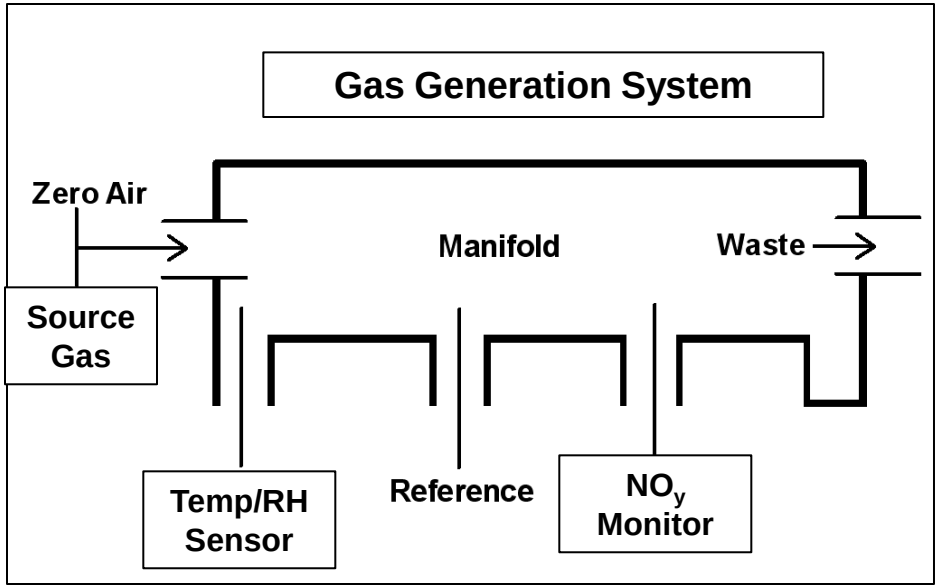
United States Environmental Protection Agency

Technical Approach



- Vibrating Orifice Aerosol Generator (VOAG) to generate test aerosols of known particle size, composition, and concentration.
- Aerodynamic Particle Sizer (APS) will be used to monitor the particles size.
- Filter pack sample will be used as a reference (IO-2 and IO-3).

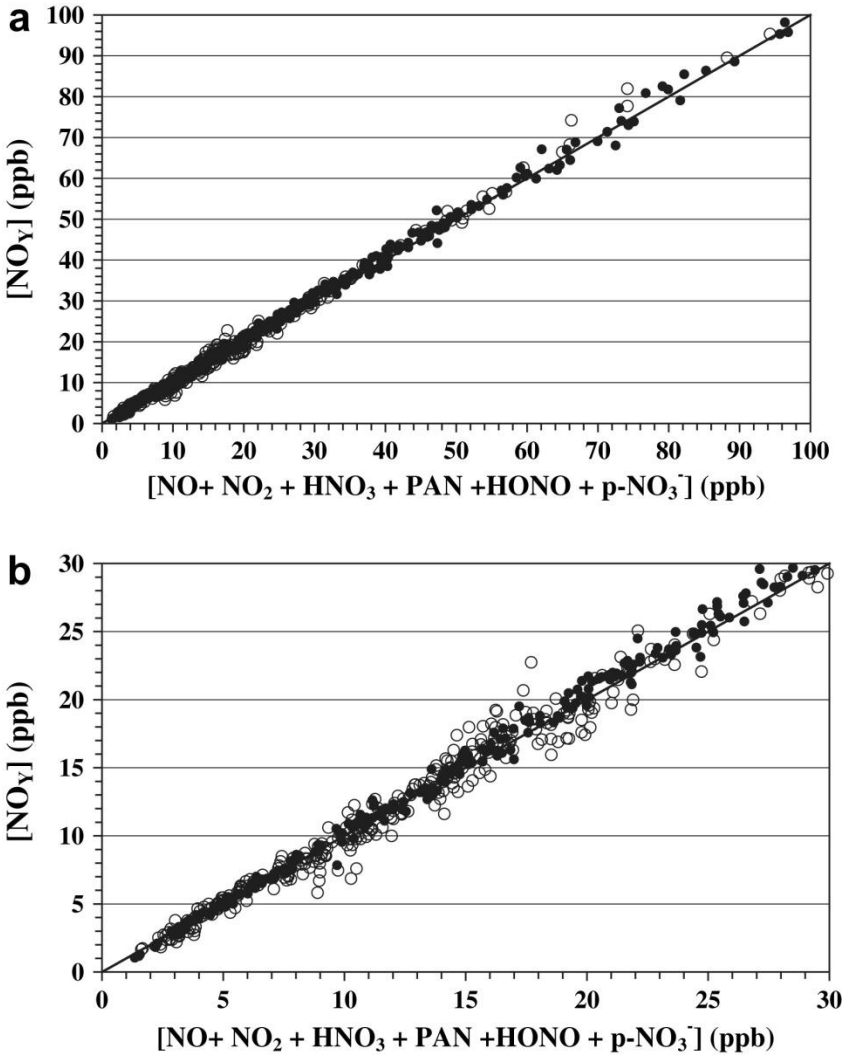
- A dynamic dilution system will be used to provide gas phase species to the candidate methods.
- Source gas from compressed gas cylinders or permeation tubes.
- Annular denuder sample will be used as a reference (IO-4).



Total Reactive Nitrogen (NO_y) FRM

United States Environmental Protection Agency

Technical Approach



- W.T. Luke et al., *Atmospheric Enviroment* 44 (2010) 4068–4080
- Scatter plot of total NO_y concentrations (ppb) and the sum of NO_y components (ppb) for day (open circles) and night (solid circles) periods during the August 15-October 2, 2006 TRAMP study in Houston, TX. A plot of the entire data set is presented in (a) and as an expanded scale in (b).

Total Reactive Nitrogen (NO_y) FRM

United States Environmental Protection Agency

Technical Approach

Table 1. Inventory of instrumentation/equipment for laboratory and ambient studies.

Instrument	Species Analyzed	Parameters Investigated
Thermo 42i-Y NO_y Monitor	NO, NO_y, NO_2+NO_z	precision, bias, Total NO_y, speciated NO_y, NO_y capture, converter efficiency/stability, vertical NO_y flux
American Ecotech 9843 NO_y Monitor	NO, NO_y, NO_2+NO_z	precision, bias, Total NO_y, speciated NO_y, NO_y capture, converter efficiency/stability, vertical NO_y flux
Teledyne API T200U NO_y Monitor	NO, NO_y, NO_2+NO_z	precision, bias, Total NO_y, speciated NO_y, NO_y capture, converter efficiency/stability, vertical NO_y flux
Teledyne API 200EU Photolytic NO_2 Monitor	NO, NO_2, NO_x	speciated NO_y
URG 9000D Ambient Ion Monitor	p-NO_3, p-NH_4, HNO_3, HNO_2, NH_3	speciated NO_y, interfering species
GC-based PAN	PAN	speciated NO_y
TSI VOAG	p-NO_3, p-NH_4	speciated NO_y, NO_y capture, converter efficiency, interfering species
Perm Tube Oven	HNO_3, NH_3	speciated NO_y, NO_y capture, converter efficiency, interfering species
Dynamic Dilution Gas Manifold	gas phase species	speciated NO_y, NO_y capture, converter efficiency, interfering species

- ORD has the capability for the high time resolution determination of the majority of the NO_y components including the most atmospherically and deposition relevant p-NO_3 and HNO_3 and the most abundant component, NO_2.

Total Reactive Nitrogen (NO_y) FRM

United States Environmental Protection Agency

Technical Approach

Establish inlet placement criteria by investigate vertical NO_y distribution

- Collocated ambient sampling with comparable instruments at differing heights along a 10m tower.
- Results compared to determine vertical NO_y concentration gradients and provide data for inlet siting criteria of the proposed FRM.

Develop calibration and challenge procedures for NO_y method Potential measurement

- Due to similarities between the NO_y method and NO_2 FRM, ORD will investigate and develop calibration procedures based upon those for the NO_2 FRM.
- The more complex composition of NO_y will result in the need for investigation and development of new procedures for challenging the NO_y FRMs calibration
  - Identification and testing of existing gases (i.e., NO_2 by GPT, IPN, and NPN) to establish representative test gases to assess the molybdenum converter efficiency.

Evaluate commercially available NO_y monitors for use as FRMs

- Ambient evaluations ~1 year in duration
- Assess the applicability of each monitor as an FRM
- Monitors will be calibrated, operated and challenged as if they were FRMs according to a detailed SOP that will be developed during the evaluation process.

Total Reactive Nitrogen (NO_y) FRM

United States Environmental Protection Agency

Schedule

- This effort began in July 2010.
- Concurrent to the NO_y FRM development and evaluation research, ORD will provide a technical summary of the available data and develop the basis/rationale for making it an FRM by May 2011.
- ORD will prepare docket materials, proposal preambles and provide a description of the proposed NO_y FRM in regulatory text format by the initial rulemaking date of July 2011. This description will use the current NO_2 FRM (40 CFR Part 50 Appendix A-1) as a template with slight modifications to account for differences between NO_2 and NO_y.
- Method evaluations will continue during the period between initial and final rule making (July 2011-March 2012).
- ORD will provide response to comments and the final FRM for NO_y in regulatory text format by the March 2012 final rule making.